

Docket No.
146154.00018



Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

TRANSPARENT, BIAXIALLY ORIENTED POLYOLEFIN FILM

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on February 3, 2000 as United States Application No. or PCT International Application Number PCT/EP00/00853 and was amended on _____

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

<u>DE 199 05 415.0</u>	<u>Germany</u>	<u>10/02/1999</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
<u> </u>	<u> </u>	<u> </u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
<u> </u>	<u> </u>	<u> </u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

Jeffrey Kushan, Reg. No. 43,401

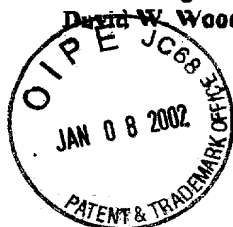
Thomas T. Moga, Reg. No. 34,880

Richard Wilder, Reg. No. 31,202

David Fitzgerald, Reg. No. 47,347

David W. Woodward, Reg. No. 35,020

I hereby appoint all of the named attorneys and each principal, attorney of counsel, associate and employee of Powell, Goldstein, Frazer & Murphy, LLP, who is a registered Patent Attorney, my attorney with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.



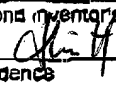
Send Correspondence to:

David W. Woodward, Powell, Goldstein, Frazer & Murphy, LLP, P.O. Box 97223,
Washington, D.C. 20004

Direct Telephone Calls to: *(name and telephone number)*

David W. Woodward (202) 624-3913

Full name of sole or first inventor	
Wolfgang RASP	
Sole or first inventor's signature	Date
Residence	
OSTERNACHER STRASSE 13, D-83209 PRIEN AM CHIEMSEE	
Citizenship	
Germany	
Post Office Address	
Same as residence	

Full name of second inventor, if any	
Detlef HÜTT	
Second inventor's signature	Date
	01.08.2001
Residence	
BREITER WEG 26, D-66265 HEUSWEILER, GERMANY	
Citizenship	
Germany	
Post Office Address	
Same as residence	

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. *(list name and registration number)*

5 Jeffrey Kushan, Reg. No. 43,401
 Thomas T. Moga, Reg. No. 34,880
 Richard Wilder, Reg. No. 31,202
 David Fitzgerald, Reg. No. 47,347
 David W. Woodward, Reg. No. 35,020

I hereby appoint all of the named attorneys and each principal, attorney of counsel, associate and employee of Powell, Goldstein, Frazer & Murphy, LLP, who is a registered Patent Attorney, my attorney with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Send Correspondence to:

David W. Woodward, Powell, Goldstein, Frazer & Murphy, LLP, P.O. Box 97223,
Washington, D.C. 20004

Direct Telephone Calls to: *(name and telephone number)*

David W. Woodward (202) 624-3913

Full name of sole or first inventor	Wolfgang RASP	
Sole or first inventor's signature	<i>[Signature]</i>	Date 2/8/2001
Residence	OSTERNACHER STRASSE 13, D-83209 PRIEN AM CHIEMSEE	
Citizenship	Germany	
Post Office Address	Same as residence	

Full name of second inventor, if any	Detlef HÜTT	
Second inventor's signature		Date
Residence	BREITER WEG 26, D-66265 HEUSWEILER, GERMANY	
Citizenship	Germany	
Post Office Address	Same as residence	

FORM PTO-1390
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

146154.00018

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

U.S. APPLICATION NO. (If known, see 37 CFR 1.5

New U.S. National Stage Patent Application

09/913118

INTERNATIONAL APPLICATION NO.
PCT/EP00/00853

INTERNATIONAL FILING DATE
February 3, 2000

PRIORITY DATE CLAIMED
February 10, 1999

TITLE OF INVENTION

TRANSPARENT, BIAXIALY ORIENTED POLYOLEFIN FILM

APPLICANT(S) FOR DO/EO/US

Wolfgang RASP and Detlef HUTT

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: PCT Request, Notification Concerning Submission or Transmittal of Priority Document and copy of the Commercial Register evidencing change of name.

U.S. APPLICATION NO. (if known, see 37 CFR 1.51) **09/913118**

INTERNATIONAL APPLICATION NO.

ATTORNEY'S DOCKET NUMBER

21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO. \$1000.00

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO \$860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =**CALCULATIONS PTO USE ONLY**

\$ 1000.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	14 - 20 =	0	x \$18.00	\$
Independent claims	1 - 3 =	0	x \$80.00	\$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$
TOTAL OF ABOVE CALCULATIONS =				\$ 1000.00

\$

\$

\$

TOTAL OF ABOVE CALCULATIONS =

\$ 1000.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
are reduced by 1/2.

+

\$

SUBTOTAL =

\$

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

TOTAL NATIONAL FEE =

\$ 1000.00

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$

TOTAL FEES ENCLOSED =

\$ 1000.00

Amount to be
refunded:

\$

charged:

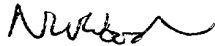
\$

- a. ☒ A check in the amount of \$ 1000.00 to cover the above fees is enclosed.
- b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
overpayment to Deposit Account No. 50-1682. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. Credit card
information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Powell, Goldstein, Frazer & Murphy LLP
P.O. Box 97223
Washington, D.C. 20090-7223
202-624-3913



SIGNATURE

David W. Woodward

NAME

35,020

REGISTRATION NUMBER

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

JC05 Rec'd PCT/PTO

08 AUG 2001

09/913118

In re Patent Application of Wolfgang RASP and Detlef HÜTT	
New U.S. National Stage Application of PCT/EP00/00853	Docket No.: 146154.00018
Filed: August 8, 2001	
For: TRANSPARENT, BIAXIALLY ORIENTED POLYOLEFIN FILM	

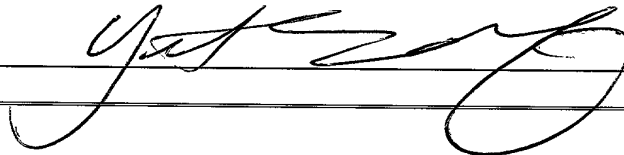
PRELIMINARY AMENDMENT

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail in an envelope addressed to: Commissioner of Patents and Trademarks, Washington, D.C. 20231 on August 8, 2001.

By



Sir:

Prior to examination of the above-identified application, Applicants respectfully request that the following amendments be entered into the application:

Changes to the Claims:

Please replace claims 3-13 with the following clean claims as follow:

3. Polyolefin film according to claim 1, characterized in that the dry-grinding process is carried out in such a way that a rough surface structure is produced.
4. Polyolefin film according to claim 1, characterized in that the ground layered silicate is non-glossy.

5. Polyolefin film according to claim 1, characterized in that the layered silicate is a mica, preferably muscovite, biotite, phlogopite, vermiculite or synthetic mica.

6. Polyolefin film according to claim 1, characterized in that the mica has optionally been ignited.

7. Polyolefin film according to claim 1, characterized in that the mean particle size is from 1 to 10 μm , preferably from 2 to 8 μm .

8. Polyolefin film according to claim 1, characterized in that the layered silicate is in the base layer and/or in one interlayer and/or in one top layer.

9. Polyolefin film according to claim 1, characterized in that the layered silicate is present in the film in a concentration of from 0.1 to 1.0 g/m^2 , preferably from 0.1 to 0.7 g/m^2 , in particular from 0.10 to 0.30 g/m^2 .

10. Polyolefin film according to claim 1, characterized in that the film has a thickness of from 3 to 10 μm , preferably from 5 to 50 μm .

11. Use of a film according to claim 1 for marking by means of a laser, preferably by means of a CO_2 laser or by means of an Nd:YAG laser or by means of an excimer laser.

12. Use of an oriented laser-marked film according to claim 1 as packaging film.

13. Process for marking a film according to claim 1 by means of a laser.

REMARKS


Entry of the foregoing amendments prior to examination is respectfully requested.

Applicants respectfully request that the foregoing amendments to claims 3-13 be entered in order to avoid this application incurring a surcharge for the presence of one or more multiple dependent claims.

A marked up version of the amended claims as required by 35 U.S.C. 1.121 is in the attached appendix.

Should there be any questions, the Examiner is invited to contact the undersigned attorney at 202-624-3913.

Respectfully submitted,



David W. Woodward
Registration No. 35,020
Attorney for Applicant

Attachment:
Appendix

POWELL, GOLDSTEIN, FRAZER & MURPHY, LLP
P.O. Box 97233
Washington, D.C. 20090-7223
202-347-0066

Date: **Wednesday, August 8, 2001**

DWW/yea

APPENDIX

Version With Markings to Show Changes Made

Changes in the Claims:

The following is a marked-up version of the amended claims:

3. Polyolefin film according to ~~Claim 1 and/or 2~~ claim 1, characterized in that the dry-grinding process is carried out in such a way that a rough surface structure is produced.
4. Polyolefin film according to ~~one or more of Claims 1 to 3~~ claim 1, characterized in that the ground layered silicate is non-glossy.
5. Polyolefin film according to ~~one or more of Claims 1 to 4~~ claim 1, characterized in that the layered silicate is a mica, preferably muscovite, biotite, phlogopite, vermiculite or synthetic mica.
6. Polyolefin film according to ~~one or more of Claims 1 to 5~~ claim 1, characterized in that the mica has optionally been ignited.
7. Polyolefin film according to ~~one or more of Claims 1 to 6~~ claim 1, characterized in that the mean particle size is from 1 to 10 μm , preferably from 2 to 8 μm .
8. Polyolefin film according to ~~one or more of Claims 1 to 7~~ claim 1, characterized in that the layered silicate is in the base layer and/or in one interlayer and/or in one top layer.
9. Polyolefin film according to ~~one or more of Claims 1 to 8~~ claim 1, characterized in that the layered silicate is present in the film in a concentration of from 0.1 to 1.0 g/m^2 , preferably from 0.1 to 0.7 g/m^2 , in particular from 0.10 to 0.30 g/m^2 .
10. Polyolefin film according to ~~one or more of Claims 1 to 9~~ claim 1, characterized in that the film has a thickness of from 3 to 10 μm , preferably from 5 to 50 μm .

11. Use of ~~one of the films~~ a film according to ~~Claims 1 to 10~~ claim 1 for marking by means of a laser, preferably by means of a CO₂ laser or by means of an Nd:YAG laser or by means of an excimer laser.
12. Use of an oriented laser-marked film according to ~~Claims 1 to 10~~ claim 1 as packaging film.
13. Process for marking a film according to ~~Claims 1 to 10~~ claim 1 by means of a laser.

- 1 -

Transparent biaxially oriented polyolefin film

The invention relates to a laser-markable, transparent, oriented polyolefin film.

The prior art discloses processes for marking polymeric materials.

- 5 Materials of this type contain a radiation-sensitive additive which causes discoloration of the material on exposure to radiation in certain wavelength ranges. These additives are known as laser pigments.

- 10 The prior art also discloses polyolefin films which are biaxially oriented for certain applications and generally have a thickness in the range from 3 to 100 μm . It is known to modify biaxially oriented films by means of suitable additives. Additives of this type may improve the friction, antistatic properties, thermal stability, appearance or other film properties. However, these additives must not impair the appearance in transparent films, i.e. in particular must not increase the haze or reduce the gloss.

- 15 The object of the present invention was therefore to provide a laser-markable, transparent, biaxially oriented polypropylene film. In particular, the film is to be markable by means of suitable processes with laser light of various wavelengths. The laser beam must not produce any through holes in the film. At the same time, the film is to have high transparency and a
20 uniform appearance without fisheyes and bubbles.

- This object is achieved by a transparent, single- or multilayer, oriented polyolefin film comprising at least one layer which comprises a layered silicate (referred to as 'the layer' below) which has an irregular surface structure and no coating of metal oxides. The sub-claims indicate preferred
25 embodiments of the invention.

The layer of the film generally comprises at least 85% by weight, preferably from 90 to < 100% by weight, in particular from 98 to < 100% by weight, in

- 2 -

each case based on the layer, of a polyolefin, preferably a propylene polymer.

Polyolefins are, for example, polyethylenes, polypropylenes, polybutylenes or copolymers of olefins having from two to eight carbon atoms, of which
5 polyethylenes and polypropylenes are preferred.

In general, the propylene polymer comprises at least 90% by weight, preferably from 94 to 100% by weight, in particular from 98 to 100% by weight, of propylene. The corresponding comonomer content of at most 10% by weight or from 0 to 6% by weight or from 0 to 2% by weight
10 respectively generally consists, if present, of ethylene and butylene. The data in % by weight are in each case based on the propylene polymer.

Preference is given to isotactic propylene homopolymers having a melting point of from 140 to 170°C, preferably from 155 to 165°C, and a melt flow index (measurement DIN 53 735 at a load of 21.6 N and 230°C) of from 1.0
15 to 10 g/10 min, preferably from 1.5 to 6.5 g/10 min. The n-heptane-soluble content of the polymer is generally from 1 to 10% by weight, preferably 2-5% by weight, based on the starting polymer.

The molecular weight distribution of the propylene polymer may vary within broad limits, depending on the area of application. The ratio between the
20 weight average molecular weight M_w and the number average molecular weight M_n is generally between 1 and 15.

In a preferred embodiment of the film according to the invention, the ratio between the weight average molecular weight M_w and the number average molecular weight M_n is from 2 to 10, very particularly preferably from 2 to 6.
25 Such a narrow molecular weight distribution of the propylene homopolymer of the layer is achieved, for example, by peroxidic degradation thereof or by

- 3 -

preparation of the polypropylene by means of suitable metallocene catalysts.

In a preferred embodiment of the invention, the polypropylene employed is highly isotactic. For highly isotactic polypropylenes of this type, the chain isotacticity index, determined by ^{13}C -NMR spectroscopy, of the n-heptane-insoluble content of the polypropylene is at least 95%, preferably from 96 to 99%.

It is essential to the invention that at least one layer of the film comprises a pigment based on layered silicate or layered silicates which has an irregular surface structure and no coating of metal oxides.

The layer generally comprises the pigment in an amount of from 0.01 to 4% by weight, preferably from 0.5 to 2.5% by weight, in particular from 0.8 to 1.5% by weight, based on the total weight of the film. It has been found that the concentration of pigment in % by weight depends on the respective layer thickness of the pigmented layer or layers. Thick layers exhibit the same effect at comparatively low concentrations as thinner layers do at higher concentrations. It is therefore preferred for the pigment concentration per area unit of the film to be in the range from 0.1 to 1.0 g/m², preferably from 0.1 to 0.7 g/m², in particular from 0.10 to 0.30 g/m². This area concentration is sufficient to ensure that the laser beam cannot pass through the film unhindered, but instead hits a pigment particle in the pigmented layer. This range for the area concentration applies irrespective of the film thickness, the layer thickness and the number of layers.

The layered silicate-based pigments are prepared from layered silicates having a platelet-shaped structure. Particularly suitable layered silicates are micas, of which muscovite, biotite, phlogopite, vermiculite and synthetic mica are particularly preferred. These starting materials, which are known

- 4 -

per se, are also used for the preparation of pearlescent pigments. For the modification of the surface structure of the layered silicates, they are subjected to a dry grinding process as described in DE 44 41 223. The conditions during the grinding process are selected in such a way that the originally smooth surface structure of the layered silicates is substantially destroyed, so that the dry-ground pigments have a rough surface structure.

In a dry-grinding process, mica, for example, is introduced into a stirred ball mill and comminuted continuously by means of grinding media, for example made of corundum. The grinding conditions can be set by the person skilled in the art without further inventive step in such a way that the platelet-shaped mica pigments are comminuted, and the originally smooth surface is considerably roughened. The platelet-shaped character of the pigment structure is retained to a certain extent in the process. All known dry-grinding processes which can be correspondingly controlled are basically suitable.

The dry-ground pigments are subsequently classified preferably by air classification. Methods of this type are known. In accordance with the state of the art, the pigments are subsequently provided with a suitable coating of metal oxides or metal oxide hydrates. A high color intensity and high hiding power of the pigments is thereby achieved. These properties are particularly desirable for many applications.

As part of the present invention, it has been noted that it is advantageous for the dry-ground pigments not to be provided with a coating of this type. The oriented films comprising an uncoated laser pigment are advantageous, since the laser marking in the form of a white mark in a transparent film is more readily visible the less the film becomes hazy, as in the case of the use of a coated pigment. In addition, the desired transparency of the oriented film comprising uncoated pigment is,

- 5 -

surprisingly, retained with virtually no change. On incorporation of coated pigments, the oriented film becomes very hazy.

It has been found that the grinding for the production of rough surfaces – but no coating with metal oxides – is essential in order to achieve a transparent, laser-markable, oriented film. It is assumed that the rough and uneven surface of the pigments that is produced by the grinding improves the adhesion of the polymers to the surface of the pigments in such a way that detachment and vacuole formation do not occur during the stretching process. Layered silicates which are coated with metal oxides after grinding cause the film to become very hazy.

It has furthermore been observed as part of the present invention that an optimum particle size for a balanced ratio of laser markability and optical properties of the film can easily be determined experimentally for a given laser pigment. The mean particle size here should not be chosen to be too small. With decreasing mean particle size, the haze of the film increases beyond an optimum mean particle size. It has furthermore been found that the laser markability is also dependent on this mean particle size. The sensitivity to the laser decreases if the wavelength of the laser light is more than a factor of 3 greater than the particle diameter. For example, the optimum mean particle size for dry-ground mica on use of a CO₂ laser is in the range from 4.5 to 5.5 µm, determined by image analysis under the electron microscope (SEM-IPS).

In addition to the laser pigments which are essential to the invention, the layer may also comprise conventional additives, such as neutralizers, stabilizers, antistatics and/or lubricants, in effective amounts in each case.

Preferred antistatics are alkali metal alkanesulfonates, polyether-modified, i.e., ethoxylated and/or propoxylated polydiorganosiloxanes (polydialkylsiloxanes, polyalkylphenylsiloxanes and the like) and/or essentially straight-

- 6 -

chain and saturated aliphatic, tertiary amines containing an aliphatic radical having 10 to 20 carbon atoms which are substituted by α -hydroxy-(C₁-C₄)alkyl groups, where N,N-bis(2-hydroxyethyl)alkylamines having 10 to 20 carbon atoms, preferably 12 to 18 carbon atoms, in the alkyl radical
5 are particularly suitable. The effective amount of antistatic is in the range from about 0.05 to 0.5% by weight. Glycerol monostearate is also preferably employed as antistatic, in an amount from 0.03% to 0.5%.

Lubricants are higher aliphatic acid amides, higher aliphatic acid esters,
10 waxes and metal soaps, and polydimethylsiloxanes. The effective amount of lubricant is in the range from 0.01 to 3% by weight, preferably from 0.02 to 1% by weight. Particularly suitable is the addition of higher aliphatic acid amides in the range from 0.01 to 0.25% by weight in the layer. A particularly suitable aliphatic acid amide is erucamide. The addition of poly-
15 dimethylsiloxanes is preferred in the range from 0.02 to 2.0% by weight, in particular polydimethylsiloxanes having a viscosity from 5000 to 1,000,000 mm²/s.

Stabilizers which can be employed are the conventional compounds having
20 a stabilizing action for polymers of ethylene, propylene and other α -olefin polymers. Their added amount is between 0.05 and 2% by weight. Particularly suitable are phenolic stabilizers, alkali metal or alkaline earth metal stearates and/or alkali metal or alkaline earth metal carbonates. Phenolic stabilizers are preferred in an amount from 0.1 to 0.6% by weight,
25 in particular from 0.15 to 0.3% by weight, and having a molecular weight of greater than about 500 g/mol. Pentaerythritol tetrakis-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate and 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene are particularly advantageous.

30 Neutralizers are preferably dihydrotalcite, calcium stearate and/or calcium carbonate having a mean particle size of at most 0.7 μ m, an absolute

- 7 -

particle size of less than 10 μm and a specific surface area of at least 40 m^2/g .

The above data in % in each case relate to the weight of the layer.

5

In a preferred embodiment, the polyolefin film according to the invention comprises top layer(s) of polymers of α -olefins having 2 to 10 carbon atoms applied to one or both sides of the laser pigment-containing layer or an interlayer.

10

Examples of α -olefinic polymers of this type of the top layer(s) are

propylene homopolymer

a copolymer of

ethylene and propylene or

15

ethylene and 1-butylene or

propylene and 1-butylene or

a terpolymer of

ethylene and propylene and 1-butylene or

a mixture of two or more of said homopolymers, copolymers and terpolymers or

20

a blend of two or more of said homopolymers, copolymers and terpolymers, if desired mixed with one or more of said homopolymers, copolymers and terpolymers,

where particular preference is given to

25

random ethylene-propylene copolymers having

an ethylene content of from 1 to 10% by weight, preferably from 2.5 to 8% by weight, or

random propylene-1-butylene copolymers having

a butylene content of from 2 to 25% by weight, preferably from 4 to 20% by weight,

30

in each case based on the total weight of the copolymer, or

- 8 -

random ethylene-propylene-1-butylene terpolymers having
an ethylene content of from 1 to 10% by weight, preferably from
2 to 6% by weight, and
a 1-butylene content of from 2 to 20% by weight, preferably from
4 to 20% by weight,
in each case based on the total weight of the terpolymer, or
a blend of an ethylene-propylene-1-butylene terpolymer and a
propylene-1-butylene copolymer
having an ethylene content of from 0.1 to 7% by weight
and a propylene content of from 50 to 90% by weight
and a 1-butylene content of from 10 to 40% by weight,
in each case based on the total weight of the polymer blend.

The above-described copolymers and/or terpolymers employed in the top
layer(s) generally have a melt flow index of from 1.5 to 30 g/10 min,
preferably from 3 to 15 g/10 min. The melting point is in the range from 120
to 140°C. The above-described blend of copolymers and terpolymers has a
melt flow index of from 5 to 9 g/10 min and a melting point of from 120 to
150°C. All the above-mentioned melt flow indices are measured at 230°C
and a force of 21.6 N (DIN 53 735).

If desired, all the above-described top-layer polymers may be peroxidically
degraded in the same manner as described above for the layer, basically
using the same peroxides. The degradation factor for the top-layer
polymers is generally in the range from 3 to 15, preferably from 6 to 10.

If desired, the additives described above for the layer, such as antistatics,
neutralizers, lubricants, and/or stabilizers, and, if desired, additionally anti-
blocking agents, can be added to the top layer(s). The data in % by weight
then relate correspondingly to the weight of the top layer.

- 9 -

Suitable antiblocking agents are inorganic additives, such as silicon dioxide, calcium carbonate, magnesium silicate, aluminum silicate, calcium phosphate and the like, and/or incompatible organic polymers, such as polyamides, polyesters, polycarbonates and the like, preference being
5 given to benzoguanamine-formaldehyde polymers, silicon dioxide and calcium carbonate. The effective amount of antiblocking agent is in the range from 0.1 to 2% by weight, preferably from 0.1 to 0.8% by weight. The mean particle size is between 1 and 6 μm , in particular 2 and 5 μm , with particles having a spherical shape, as described in EP-A-0 236 945 and
10 DE-A-38 01 535, being particularly suitable.

The film according to the invention comprises at least one layer comprising laser pigments. This pigment-containing layer is preferably the base layer of a three- or five-layered embodiment. If desired, the pigment-containing
15 layer may also be the interlayer of a four- or five-layered embodiment. In a further embodiment, pigments are incorporated both into the base layer and into the interlayer. A further variant of the invention is a structure in which the top layer, in addition to the pigment-containing base layer and/or interlayer, also comprises laser pigments.

20

The thickness of the top layer(s) is greater than 0.1 μm and is preferably in the range from 0.3 to 3 μm , in particular from 0.4 to 1.5 μm , where top layers on both sides may have identical or different thicknesses.

25 The interlayer(s) may consist of the α -olefinic polymers described for the base layer. The interlayer(s) may comprise the conventional additives described for the individual layers, such as antistatics, neutralizers, lubricants and/or stabilizers, and, if desired, additionally antiblocking agents. The thickness of the interlayer(s) is greater than 0.3 μm and is
30 preferably in the range from 1.0 to 15 μm , in particular from 1.5 to 10 μm .

- 10 -

The total thickness of the polyolefin film according to the invention can vary within broad limits and depends on the intended use. It is preferably from 4 to 60 μm , in particular from 5 to 50 μm , preferably from 10 to 35 μm , the layer making up about 40 to 100% of the total film thickness.

5

The invention furthermore relates to a process for the production of the polyolefin film according to the invention by the coextrusion process, which is known per se.

10 This process is carried out by coextruding the melts corresponding to the individual layers of the film through a flat-film die, taking off the resultant film over one or more roll(s) for solidification, subsequently stretching (orienting) the film, heat-setting the stretched film and, if desired, corona- or heat-treating the surface layer intended for the treatment.

15

The biaxial stretching (orientation) is generally carried out sequentially or simultaneously. The sequential stretching is generally consecutively, with consecutive biaxial stretching, in which stretching is firstly carried out longitudinally (in the machine direction) and then transversely (perpendicular to the machine direction), being preferred. The simultaneous stretching can be carried out by the flat film process or by the blowing process. The further description of the film production relates to the example of flat film extrusion with subsequent sequential stretching.

20

25 Firstly, as is conventional in the coextrusion process, the polymer or polymer mixture of the individual layers is compressed and liquefied in an extruder, it being possible for the laser pigments and any other additives optionally added already to be present in the polymer or polymer mixture. The melts are then forced simultaneously through a flat-film die (slot die),
30 and the extruded multilayer film is taken off on one or more take-off rolls, during which it cools and solidifies.

- 11 -

The film obtained in this way is then stretched longitudinally and transversely to the extrusion direction, which results in alignment of the molecule chains. The longitudinal stretching is advantageously carried out with the aid of two rolls running at different speeds corresponding to the target stretching ratio, and the transverse stretching is advantageously carried out with the aid of an appropriate tenter frame. The longitudinal stretching ratios are in the range from 4 to 8, preferably from 5 to 6. The transverse stretching ratios are in the range from 5 to 10, preferably from 7 to 9.

The stretching of the film is followed by heat-setting (heat treatment) thereof, in which the film is held at a temperature from 100 to 160°C for from about 0.1 to 10 seconds. The film is subsequently wound up in a conventional manner by means of a wind-up unit.

It has proven particularly favorable to keep the take-off roll or rolls by means of which the extruded film is cooled and solidified at a temperature from 10 to 100°C, preferably from 20 to 50°C, by means of a heating and cooling circuit.

The temperatures at which longitudinal and transverse stretching are carried out can vary in a relatively broad range and depend on the desired properties of the film. In general, the longitudinal stretching is preferably carried out at from 80 to 150°C and the transverse stretching is preferably carried out at from 120 to 170°C.

After the biaxial stretching, one or both surface(s) of the film is/are preferably corona- or flame-treated by one of the known methods. The treatment intensity is generally in the range from 37 to 50 mN/m, preferably from 39 to 45 mN/m.

- 12 -

The surface treatment of the film is described here using the example of corona treatment.

- 5 In the corona treatment, an advantageous procedure is to pass the film between two conductor elements serving as electrodes, with such a high voltage, usually an alternating voltage (from about 5 to 20 kV and from about 5 to 30 kHz), being applied between the electrodes that spray or corona discharges are able to occur. Due to the spray or corona discharge, the air above the film surface ionizes and reacts with the molecules of the film surface, causing formation of polar inclusions in the essentially non-polar polymer matrix.

- The film according to the invention can be laser-inscribed by processes known per se. For this purpose, the film is introduced into the beam path of a pulsed laser, preferably a pulsed CO₂ laser or an Nd:YAG or excimer laser. The choice of laser depends on the wavelength at which the pigment has the highest possible absorption cross section. The shade and color intensity of the marking depend on the irradiation time and the energy density of the radiation.

The raw materials and films were characterized using the following measurement methods:

25 Melt flow index

The melt flow index was measured in accordance with DIN 53 735 at a load of 21.6 N and 230°C.

Mean particle size

- 30 The mean particle size was determined by image analysis. For this purpose, a sample is dispersed in water in order to separate the particles

- 13 -

and is applied to a glass slide. The sample is subsequently dried and examined under the scanning electron microscope. For this purpose, the individual particles are visualized as gray shade image by means of a suitable setting of brightness and contrast. Over an area of 10 mm², the
5 respective area of the separated particles is measured, and the particle diameter is given as the diameter of a circle of equal area. These measurement values are classified by size ranges and indicate the distribution of the particle size. The mean particle diameter is determined as the mean of the distribution curve.

10

Melting Point

DSC measurement, maximum of the melting curve, heating rate 20°C/min.

Haze

15 The haze of the film was measured in accordance with ASTM-D 1003-52.

Gloss

The gloss was determined in accordance with DIN 67 530. The reflector value was measured as an optical parameter for the surface of a film. In
20 accordance with the standards ASTM-D 523-78 and ISO 2813, the angle of incidence was set at 60°. A light beam hits the planar test surface at the set angle of incidence and is reflected or scattered thereby. The light beams incident on the photoelectronic receiver are displayed as a proportional electrical quantity. The measurement value is dimensionless and must be
25 specified together with the angle of incidence.

Molecular weight determination

The mean molecular weights Mw and Mn and the mean molecular weight dispersity Mw/Mn were determined in accordance with DIN 55 672, Part 1,
30 by means of gel permeation chromatography. Instead of THF, ortho-dichlorobenzene was used as eluent. Since the olefinic polymers to be

- 14 -

investigated are insoluble at room temperature, the entire measurement is carried out at elevated temperature ($\approx 135^{\circ}\text{C}.$).

The invention is explained below by working examples.

Preparation of dry-ground mica:

- 5 Naturally occurring mica having a platelet diameter of about 2 μm was dry-ground in an industrial stirred ball mill with corundum grinding elements having a diameter of 5 mm. The ground material was subsequently classified in an air classifier in such a way that a fraction having a mean particle diameter of about 5 μm and a cut-off of 15 μm was obtained. The
- 10 pigments obtained in this way were incorporated directly, i.e. without further metal oxide coating, into propylene homopolymer having a melting point of 166°C and a melt flow index of 3.4 g/10 min. In this way, a masterbatch comprising 60% by weight of propylene homopolymer and 40% by weight of dry-ground, metal oxide-free mica (referred to as laser pigment below)
- 15 was obtained.

Example 1

- A transparent five-layered film having a symmetrical structure and a total thickness of 30 μm was produced by coextrusion followed by stepwise orientation in the longitudinal and transverse directions. The top layers
- 20 each had a thickness of 0.7 μm . The interlayers each had a thickness of 5 μm .

Base layer:

- 96.74% by weight of isotactic propylene homopolymer having a melting point of 166°C and a melt flow index of 3.4 g/10 min
- 25 3.00% by weight of the above-described masterbatch comprising 60% by weight of propylene homopolymer and 40% by

weight of the laser pigment, corresponding to a content
of 1.2% by weight of laser pigment, based on the layer,
0.14% by weight of Armostat
0.12% by weight of erucamide

5 Interlayers:

100% by weight of isotactic propylene homopolymer having a melting
point of 166°C and a melt flow index of 3.4 g/10 min

Top layers:

10 98.8% by weight of random ethylene-propylene-butylene terpolymer
having an ethylene content of 3% by weight and a
butylene content of 7% by weight (remainder
propylene)
0.2% by weight of SiO₂ as antiblocking agent, having a mean particle
size of 2 µm

15 The production conditions in the individual process steps were as follows:

20	Extrusion:	Temperatures	Base layer:	260°C
			Interlayers:	255°C
			Top layers:	240°C
			Temperature of the take-off rolls:	20°C
20	Longitudinal stretching:	Temperature:		110°C
		Longitudinal stretching ratio:		5.5
	Transverse stretching:	Temperature:		160°C
		Transverse stretching ratio:		9
25	Setting:	Temperature:		150°C
		Convergence:		5%

Example 2

A film was produced as described in Example 1. In contrast to Example 1, however, the film contained no interlayers. The film thickness of the three-layered embodiment was therefore only 20 μm . The remainder of the composition and the production conditions were unchanged compared with Example 1.

Example 3

A film was produced as described in Example 1. In contrast to Example 1, the base layer contained no laser pigment. Instead, laser pigment in an amount of 2.2% by weight, based on the weight of the layer, was incorporated into the interlayer via the 40% masterbatch (i.e. 5.6% of masterbatch). The remainder of the composition and the production conditions were unchanged compared with Example 1.

Example 4

A film was produced as described in Example 1. In contrast to Example 1, 1.95% by weight of the 40% masterbatch, corresponding to a content of 0.78% by weight, based on the weight of the base layer, were incorporated into the base layer. In addition, 1.95% by weight of the 40% masterbatch were incorporated into the respective interlayers, corresponding to a content of 0.78% by weight, based on the weight of the respective interlayer. The remainder of the composition and the production conditions were unchanged compared with Example 1.

Example 5

A film was produced as described in Example 2, with the base layer now comprising only 0.6% by weight of the laser pigment. The remainder of the composition and the production conditions were unchanged compared with Example 2.

Comparative Example 1

A film was produced as described in Example 1. In contrast to Example 1, the film now contained a wet-ground mica having a smooth platelet-shaped structure instead of the dry-ground mica having a rough surface and no metal oxide coating. For the wet grinding, a moist suspension of the platelet-shaped mica is ground between two surfaces moved relative to one another. The mica was principally comminuted by shear forces here, with the original platelet shape being substantially retained. The mean particle diameter of the wet-ground mica was likewise about 5 μm , with a cut-off of 15 μm . The remainder of the composition and the production conditions were unchanged compared with Example 1.

Comparative Example 2

A film was produced as described in Example 1. In contrast to Example 1, the film now contained a dry-ground mica with TiO_2 coating instead of the dry-ground mica having a rough surface and no metal oxide coating. For this purpose, the mica was suspended in water after dry grinding (as described above) and warmed to about 75°C with stirring. A pH of 2.2 is set by means of 10% hydrochloric acid. TiCl_4 solution was subsequently added to the mica suspension, with the pH being kept constant by means of 32% sodium hydroxide solution. When the TiCl_4 solution has been added, a pH of 7 is set using sodium hydroxide solution, and stirring is continued. The mixture is subsequently washed chloride-free with water and dried at 110°C. The pigments were subsequently ignited at about 700°C for 1 hour. The remainder of the composition and the production conditions were unchanged compared with Example 1.

The films produced in accordance with the examples and comparative examples were irradiated for 0.2 μsec by means of a CO_2 laser at a wavelength of 9.3 μm and an energy density of from 5 to 7 J/cm^2 and

- 18 -

marked with a bar code. The results from the examples and comparative examples are shown in the table below.

TABLE 1
RESULTS OF THE EXAMPLES AND COMPARATIVE EXAMPLES

- 19 -

TABLE

	Appearance	Haze in accordance with ASTM 1003-52	Gloss in accordance with DIN 67 530 at 60°	Laser marking CO ₂ laser	Laser pigment
E1	++	8	140	+++	1.2% by wt. in the base layer
E2	+++	5	145	+++	1.2% by wt. in the base layer
E3	+	12	120	+++	2.2% by wt. in the interlayer
E4	+++	7	140	+++	No interlayer
E5	+++	4	145	++	0.78% by wt. in the base layer and interlayer
CE1	Spots, microvoiding	15-20 irregular	120 -- 140 irregular	+++	0.6% by wt. in the base layer
CE2	-- Microvoiding	20	140	+++	Wet grinding Metal oxide coating after grinding

E = Example, CE = Comparative Example

- 20 -

Patent Claims

1. Transparent, single- or multilayered, oriented polyolefin film comprising at least one layer, characterized in that the film comprises in at least one layer a layered silicate which has an irregular surface structure and no coating of metal oxides.
5
2. Polyolefin film according to Claim 1, characterized in that the platelet-shaped layered silicate is subjected to a dry-grinding process.
3. Polyolefin film according to Claim 1 and/or 2, characterized in that the dry-grinding process is carried out in such a way that a rough surface structure is produced.
10
4. Polyolefin film according to one or more of Claims 1 to 3, characterized in that the ground layered silicate is non-glossy.
5. Polyolefin film according to one or more of Claims 1 to 4, characterized in that the layered silicate is a mica, preferably muscovite, biotite, phlogopite, vermiculite or synthetic mica.
15
6. Polyolefin film according to one or more of Claims 1 to 5, characterized in that the mica has optionally been ignited.
7. Polyolefin film according to one or more of Claims 1 to 6, characterized in that the mean particle size is from 1 to 10 μm , preferably from 2 to 8 μm .
20

- 21 -

8. Polyolefin film according to one or more of Claims 1 to 7, characterized in that the layered silicate is in the base layer and/or in one interlayer and/or in one top layer.
- 5 9. Polyolefin film according to one or more of Claims 1 to 8, characterized in that layered silicate is present in the film in a concentration of from 0.1 to 1.0 g/m², preferably from 0.1 to 0.7 g/m², in particular from 0.10 to 0.30 g/m².
- 10 10. Polyolefin film according to one or more of Claims 1 to 9, characterized in that the film has a thickness of from 3 to 100 µm, preferably from 5 to 50 µm.
11. Use of one of the films according to Claims 1 to 10 for marking by means of a laser, preferably by means of a CO₂ laser or by means of an Nd:YAG laser or by means of an excimer laser.
- 15 12. Use of an oriented laser-marked film according to Claims 1 to 10 as packaging film.
13. Process for marking a film according to Claims 1 to 10 by means of a laser.
- 20 14. Process for the production of a polyolefin film according to Claim 1, characterized in that the orientation in the longitudinal direction is carried out with a longitudinal stretching ratio of from 3:1 to 9:1 and/or the orientation in the transverse direction is carried out with a transverse stretching ratio of from 4:1 to 10:1.

Docket No.
146154.00018

Declaration and Power of Attorney For Patent Application

English Language Declaration

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

TRANSPARENT, BIAXIALLY ORIENTED POLYOLEFIN FILM

the specification of which

(check one)

☐ is attached hereto.

☒ was filed on February 3, 2000 as United States Application No. or PCT International Application Number PCT/EP00/00853 and was amended on _____

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)

Priority Not Claimed

<u>DE 199 05 415.0</u>	<u>Germany</u>	<u>10/02/1999</u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
<u> </u>	<u> </u>	<u> </u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	
<u> </u>	<u> </u>	<u> </u>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	

I hereby claim the benefit under 35 U.S.C. Section 119(e) of any United States provisional application(s) listed below:

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U. S. C. Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. Section 112, I acknowledge the duty to disclose to the United States Patent and Trademark Office all information known to me to be material to patentability as defined in Title 37, C. F. R., Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)
(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.